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Comments on "Kinetic Study on the Hexacelsian-Celsian Phase Transformation"

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November 1992

NASA
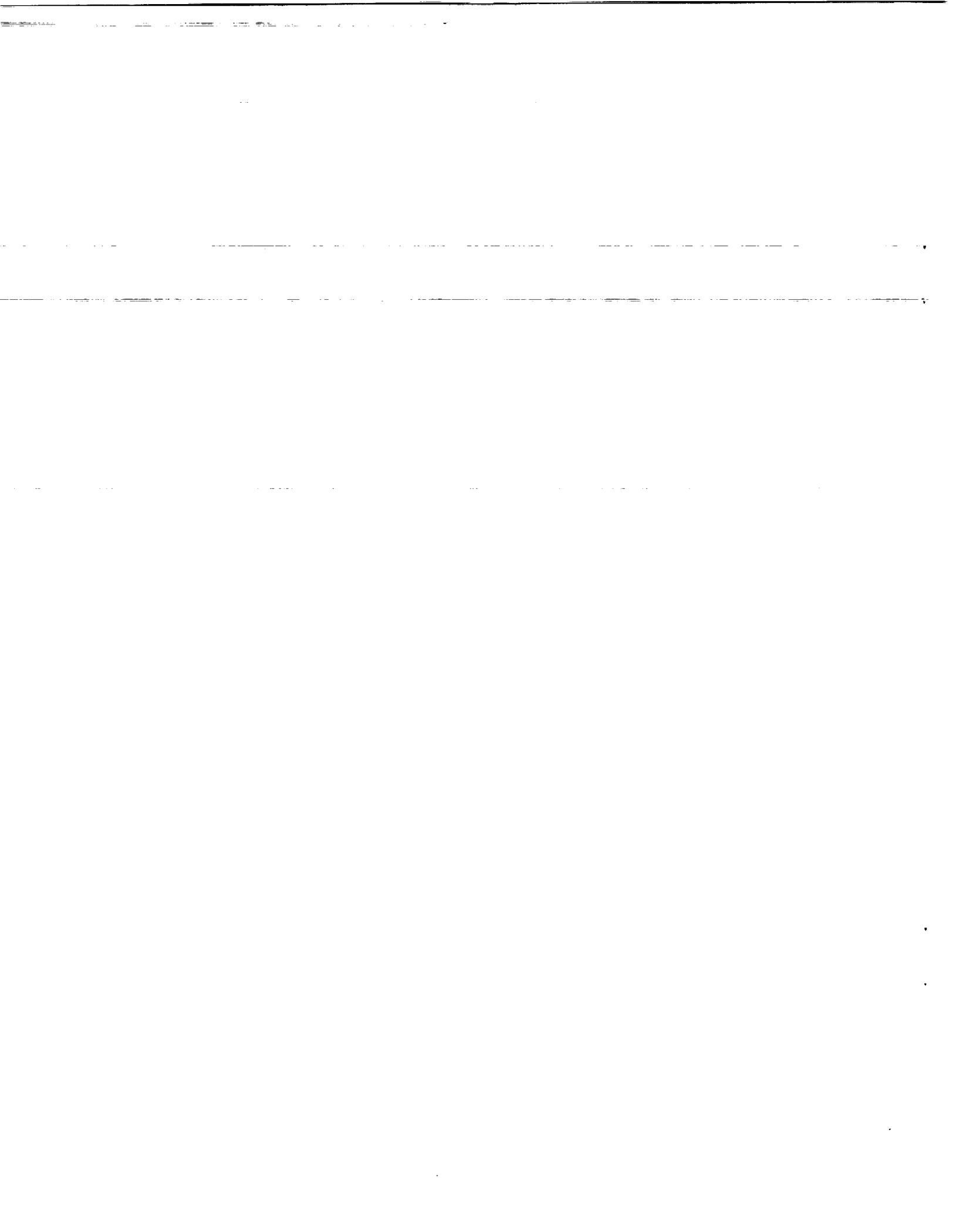
Comments on

"Kinetic Study on the Hexacelsian-Celsian Phase Transformation"
by D. Bahat, J. Mater. Sc., 5 (1970) 805-810

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Bahat [1] studied the hexacelsian-celsian phase transformation in crystallized grains of amorphous $BaAl_2Si_2O_8$. For the first stage, the transformation was reported to be controlled by the crystal growth rate. The activation energy for this transformation was evaluated to be 20.1 $\pm$ 4 kcal/mole. It was suggested that this transformation does not involve Si-O and Al-O bond openings, since this would require an activation energy of 60 kcal/mole or higher for a bond breaking mechanism.

In recent investigations, the present authors [2,3] have reported a value of 125 kcal/mole for the activation energy of hexacelsian-to-celsian transformation in the Sr- analogue, $SrAl_2Si_2O_8$. Furthermore, since the transformation involves a structural change, from a double-layered sandwich structure of

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hexacelsian to a three-dimensional framework structure of celsian, Si-O and Al-O bond breaking would be necessary for such a transformation. There appears to be a significant discrepancy between the results of the study by Bahat [1] and the requirements of the structural transformation from hexacelsian to celsian.

In an effort to understand the cause of this discrepancy, the experimental results of Bahat [1] have been analyzed using the Avrami equation [4]:

$$x = 1 - \exp[-(kt)^n] \tag{1}$$

where x is the volume fraction transformed after time t, k is the reaction rate constant, and n is the Avrami exponent which determines the geometry for interface and diffusion controlled mechanisms. Rearranging eq. (1) and taking logarithm gives

$$\ln[-\ln(1-x)] = n \ln k + n \ln t \tag{2}$$

Data from Figure 4 of Bahat's paper [1] were read and analyzed using eq. (2) in the form of plots of $\ln [-\ln(1-x)]$ vs. $\ln t$ (Figure 1) at six different temperatures ranging from 1050 to 1300 °C and times from 0.5 - 8 hours. The values of n and k at various temperatures were evaluated from linear regression analysis of the data and are listed in Table I. An average value of n close to 0.5 suggests [5] the possibility of a diffusion controlled growth with a plate geometry.

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Temperature dependence of k is expressed by the Arrhenius equation:

$$k = \nu \exp[-E/RT] \qquad (3)$$

where ν is the frequency factor, E the activation energy, R the gas constant, and T the isothermal reaction temperature in Kelvin. Arrhenius plots of $\ln k$ vs. $1/T$ for the data of Table I are shown in Figure 2. A linear regression analysis of the data (the 1050 and 1300 °C data excluded) gave a value of 89 ± 14[1] kcal/mole for E and $\nu = 5 \times 10^8/s$, with correlation coefficient of -0.977. Least-squares linear regression analysis of five data points (the 1050 °C data excluded) resulted in 65 ± 17[1] kcal/mole for E, $\nu = 1.05 \times 10^5/s$, with correlation coefficient of -0.913 indicating a poorer fit. When all the six data points are used in the statistical analysis, a lower value of activation energy is obtained, but the 1050 °C data lies outside the 95% confidence interval.

Plots of hexacelsian (weight %) vs. time, when extrapolated to t = 0, should result in zero per cent transformation since the starting material was 100% hexacelsian in all cases. But the data in Figure 4 of Bahat's paper do not extrapolate to 100% hexacelsian at zero time of heat treatments. Furthermore, these extrapolated values at t = 0, were taken as the values of reaction rate constants k at various temperatures by Bahat which is not correct.

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[1]one standard deviation

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The activation energy of hexacelsian-to-celsian transformation in $BaAl_2Si_2O_8$, obtained by reanalysis of Bahat's data using the Avrami equation, is significantly greater than the value of 20.1 $\pm$ 4 kcal/mole reported by Bahat. The recalculated values of E appear to be more reasonable and are consistent with a mechanism which involves breaking of the Al-O and/or Si-O bonds. The breaking of these bonds would be necessary for transformation of a layered hexacelsian structure into a three-dimensional feldspar structure of celsian. These values are also in better agreement with a value of 60 kcal/mole, the energy required for the ordering of albite [6] which involves Si-O and Al-O bond openings.

A further study is needed to obtain a more reliable value of the activation energy. We are presently investigating the kinetics of hexacelsian-celsian phase transformation using a quantitative X-ray diffraction technique and the results of this study would be reported in the near future.

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3. C. H. Drummond, III and N. P. Bansal, "Phase Transformations in $SrAl_2Si_2O_8$ Glass," to be Presented at XVI International Congress on Glass, Madrid, Spain, October 4 - 9, 1992; NASA Technical Memorandum 10567.

4. M. Avrami, J. Chem. Phys., **7** (1939) 1103.

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TABLE I. Values[a] of Avrami Parameter, n, and Reaction Rate
Constant, k, for Hexacelsian-to-Celsian Transformation
in $BaAl_2Si_2O_8$ at Various Temperatures

| Temperature ($^\circ$ C)	k x 10^6 (s^{-1})	n
1050	20.9	1.4
1100	3.7	0.37
1150	7.2	0.38
1200	41.8	0.62
1250	73.3	0.79
1300	48.9	0.54

[a]Calculated from data of Bahat [1]
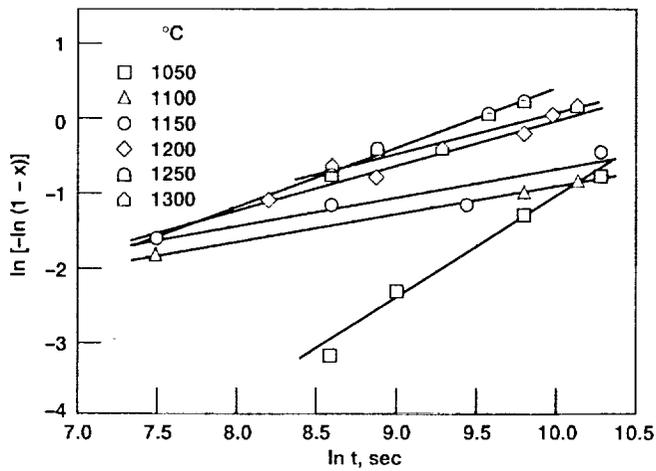
Figure 1.—Avrami plots at various temperatures for hexacelsian to celsian transformation for $BaAl_2Si_2O_8$. (Data read from Fig. 4 of Bahat's paper [1]).
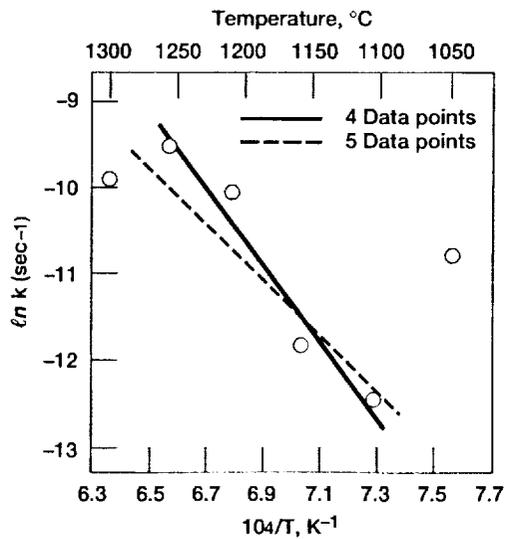

Figure 2.—Arrhenius plots of ln k vs. 1/T for hexacelsian to celsian transformation in $BaAl_2Si_2O_8$. The lines are from linear regression analysis. The 1050 and 1300 °C data excluded for the solid line and the 1050 °C data dropped for the broken line.

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	November 1992	Technical Memorandum

4. TITLE AND SUBTITLE

Comments on "Kinetic Study on the Hexacelsian-Celsian Phase Transformation"

5. FUNDING NUMBERS

WU-510-01-50

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
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8. PERFORMING ORGANIZATION REPORT NUMBER

E-7408

9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, D.C. 20546-0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM-105917

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Category 27

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Bahat (J. Mater. Sc., 5, 805 (1970)) reported a value of 20.1 ± 4 kcal/mole for the activation energy (E) for the hexacelsian to celsian phase transformation in $BaAl_2Si_2O_8$. In the present work, Bahat's experimental data have been reanalyzed and a much higher value of E has been obtained. This revised E value is consistent with the transformation mechanism of a layered hexacelsian structure into a three-dimensional feldspar structure of celsian which would necessitate the breaking of the Si-O and/or the Al-O bonds.

14. SUBJECT TERMS

Kinetics; Celsian; Hexacelsian; Phase change

15. NUMBER OF PAGES

8

16. PRICE CODE

A02

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	